

## DRAWINGS ATTACHED



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## (54) HYDROFORMYLATION PROCESS

- (71) We, BP CHEMICALS LIMITED, of Britannic House, Moor Lane, London, E.C.2., a British company, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—
- This invention relates to a novel process for the hydroformylation of olefins to give aldehydes.
- The oxo process, also known as hydroformylation, of reacting an olefin with carbon monoxide and hydrogen at elevated temperature and pressure to give as products aldehydes and/or alcohols, is well known. Cobalt compounds particularly the octacarbonyl are the most commonly used catalysts, but a number of other transition metal compounds such as rhodium complex compounds can also be employed. The reaction is carried out in a high pressure reactor which on the industrial scale is normally operated continuously. Olefin, carbon monoxide and hydrogen feeds are continuously fed under pressure into the reactor which contains a liquid reaction mixture comprising the complex organic catalyst in solution. Part of the reaction mixture, containing the aldehyde and alcohol products and a certain amount of high boiling material formed in the reaction, is continuously withdrawn from the reactor in the vapour phase and after condensation is subjected to a series of distillation stages to separate from the higher boiling residues the aldehyde and alcohol products. It is also necessary to prevent the higher boiling material from accumulating in the reactor and this, conventionally, is carried out by withdrawing a liquid purge stream from the reactor which contains catalyst, high boiling material and a certain amount of aldehyde and alcohol product. This liquid purge stream is also passed to the series of distillation stages and thereby the aldehyde and alcohol products are recovered. The catalyst removed in the purge stream, however, leaves the final distillation stage as a solution in the high boiling material. It is then necessary either to further process this solution to recover the catalyst for recycle to the reactor or to maintain the catalyst concentration in the reactor by adding a catalyst make-up stream.
- According to the present invention a process for the production of aldehydes comprises continuously feeding an olefin, carbon monoxide and hydrogen to a reaction mixture maintained at elevated temperature and pressure and containing a catalyst which is a complex of a Group VIII metal other than iron, nickel, palladium or platinum, continuously withdrawing from the reactor a vapour product stream overhead from which aldehyde product is separated by fractional distillation, continuously withdrawing from the reactor a liquid stream comprising the complex catalyst, aldehyde and high boiling residues, passing the liquid stream under reaction pressure over the surface of a membrane such that a proportion of the high boiling residues and aldehydes permeates through the membrane and is removed, and recycling the remainder of the liquid stream containing the catalyst to the reactor.
- The process of the invention has several advantages. Firstly, it is now unnecessary to further process the catalyst solution in the high boiling material leaving the final distillation stage in order to recycle the catalyst to the reactor. It is also unnecessary to add make-up catalyst to the reactor to compensate for that rejected in said high boiling material leaving the final distillation stage. A further advantage is that the separation from the liquid reaction mixture which contains the complex catalyst of a proportion of the higher boiling residues takes place under the same partial pressure of carbon monoxide as is present in the reactor. This

reduces the loss of expensive catalyst by deactivation and precipitation of catalyst metal which tends to occur when the carbon monoxide partial pressure is reduced for instance as is the case where the aldehyde reaction product is removed from the reactor in a liquid stream and subsequently distilled for separation of the aldehyde product.

The catalysts used in the process of the present invention are preferably complexes of cobalt, rhodium or ruthenium and it is particularly preferred to carry out the process using the catalysts and processes described in our British Patent Specification Nos. 1243189, 1263720, 1248988, 1281389, 1284615 and British Application No. 7308/70. The most preferred catalysts are the rhodium beta-diketonate catalysts described in British Patent Specification No. 1243189 particularly those derived from acetylacetonate.

In the hydroformylation process according to the present invention the olefin feed may comprise olefins having between 2 and 20 carbon atoms per molecule and particularly ethylene, propylene, hexenes, heptenes and octenes. The double bond is preferably terminal but one may be internal.

The hydrogen to carbon monoxide ratio in the feed may be between 20:1 and 1:4.

The catalyst:olefin ratio will vary depending on the catalyst used but is suitably between 1:20 and 1:25,000,000 moles catalyst per mole of the olefin feed, and preferably between 1:20,000 and 1:5,000:000 moles per mole of feed. The catalyst may be introduced dissolved in a solvent or in the feed or recycled product. The solvent may be a saturated or aromatic hydrocarbon. Normal paraffins such as n-hexane, n-heptane and n-octane are suitable.

The hydroformylation is suitably carried out at a pressure between 0 and 4000 psig, preferably between 0 and 2000 psig. Suitably the temperature is between 20°C and 250°C, and preferably between 60°C and 180°C.

The process of the present invention is described in more detail with reference to the accompanying drawing which shows schematically the various units employed.

Referring to the drawing, an olefin, hydrogen and carbon monoxide are reacted in a reactor (1) in the presence of a metal complex catalyst. A vapour product stream is continuously withdrawn from the reactor as an overhead fraction through a line (2), which fraction is then treated in one or more separation stages (not shown), to recover the aldehyde product. Suitably this is carried out by passing the overhead fraction to a condenser where aldehydes and alcohols are condensed, the remainder of the gaseous fraction containing excess olefin being recycled to the reactor, and the liquid product

from the condenser is then passed to a fractional distillation column, in which aldehydes are recovered as an overhead fraction.

A liquid stream containing the catalyst and high boiling residues in solution in the reaction mixture is continuously withdrawn from the reactor through a line (3), passed through circulating pump (4) and heat exchanger (5) fed with cooling water and allowed to flow under reaction pressure over a membrane unit (6) to separate a proportion of the high boiling residues and aldehyde from the catalyst, which proportion is then discharged from the reactor through line 7. A catalyst enriched stream is recycled to the reactor through line 8. The membrane is chosen so that on bringing the mixture into contact with one side of the membrane at an applied pressure greater than the pressure on the opposite side of the membrane, the pressure differential being greater than the osmotic pressure of the system, the permeate has a reduced content of the metal complex catalyst. Suitable membranes include cellulosic membranes e.g. cellulose acetate, as described in our British Patent Specification No. 1243507, silicone rubber membranes as described in our British Patent Specification No. 1243508, poly-olefin membranes as described in our British Patent Specification No. 1260733 and polyamide membranes as described in our British Patent Specification No. 1266180. The surface area of the membrane and the rate of the permeate stream may be adjusted so that the level of high boiling residues in the reaction mixture in the reactor remains constant.

Using the unit assembly described above various metal complex catalyst were separated from high boiling residues as is described in more detail in the following Examples.

#### Example 1

The rhodium complex  $\text{Rh}(\text{CO})_2$  acetylacetonate ( $\text{PBU}_2$ ) was separated from the high boiling material produced in the conversion of propylene to butyraldehyde using a cellulose acetate membrane made by Sartorius\*, Germany having pore sizes in the region 50-100Å. The separation was carried out at 68.9 bar (1000 psig) and ambient temperature over a period of 763.7 hr. The membrane retained between 78-94.3% of the rhodium complex in the feed stream and permeated the rhodium complex-depleted fraction at a rate of 2.1-0.3 mm/hr.

#### Example 2

The rhodium complex  $\text{Rh}(\text{CO})_2$  acetylacetonate was separated from a mixture of propionaldehyde and aldol condensation products of propionaldehyde using a silicone rubber membrane. The mixture was representative of the liquid purge removed from

the reactor in the conversion of ethylene to propionaldehyde and contained 40% w/w propionaldehyde, 60% w/w added condensation products of propionaldehyde with 25 ppm rhodium present in the form  $\text{Rh}(\text{CO})_2$  acetyl acetate.

Prior to use the silicone rubber membrane was pressurized with water in a reverse osmosis cell at 41.3 bar (600 psig) for several hours. The separation was carried out at 103 bar (1500 psig) and ambient temperature for a period of 159 hrs. The membrane retained between 60% and 50% of the rhodium in the feed and permeated the rhodium depleted fraction at a rate of 0.47-0.20 mm/hr.

### Example 3

The rhodium complex  $\text{Rh}(\text{CO})_2$  acetyl acetate was separated from a mixture of propionaldehyde and aldol condensation products of propionaldehyde using a membrane of mixed cellulose esters made by Millipore\* and having a molecular weight of 1000. The mixture was representative of the liquid purge removed from the reactor in the conversion of ethylene to propionaldehyde and contained 40% w/w propionaldehyde with 75 ppm rhodium present in the form  $\text{Rh}(\text{CO})_2\text{acac}$ . The separation was carried out at 103 bar (1500 psig) and ambient temperature for a period of 7 hrs. The membrane retained 93-87% of the rhodium in the feed stream and permeated the rhodium depleted fraction at a rate of 0.5 mm/hr.

### WHAT WE CLAIM IS:—

1. A process for the production of aldehydes which comprises continuously feeding an olefin, carbon monoxide and hydrogen to a reaction mixture maintained at elevated temperature and pressure and containing a catalyst which is a complex of a Group VIII metal other than iron, nickel, palladium or platinum, continuously withdrawing from the reactor a vapour product stream overhead from which aldehyde product is separated by fractional distillation, continuously withdrawing from the reactor a liquid stream comprising the complex catalyst, aldehyde and high boiling residues, passing the liquid stream under reaction pressure over the surface of a membrane such that a proportion of the high boiling residues and aldehyde permeates through the membrane and is removed, and recycling the remainder of the liquid stream containing the catalyst to the reactor.

2. A process as claimed in claim 1 wherein the reaction mixture is maintained under an elevated pressure of between 0 and 4000 psig.

3. A process as claimed in claim 2 wherein the reaction mixture is maintained under an elevated pressure of between 0 and 2000 psig.

4. A process as claimed in any one of the preceding claims wherein the membrane is a cellulosic membrane.

5. A process as claimed in claim 4 wherein the membrane is a cellulose acetate membrane.

6. A process as claimed in any one of claims 1 to 3 wherein the membrane is a silicone rubber membrane.

7. A process as claimed in any one of claims 1 to 3 wherein the membrane is a polyolefin membrane.

8. A process as claimed in any one of claims 1 to 3 wherein the membrane is a polyamide membrane.

9. A process for the production of aldehydes as claimed in claim 1 substantially as hereinbefore described with reference to the accompanying drawing.

10. A process for the production of aldehydes as claimed in claim 1 substantially as hereinbefore described with reference to the examples.

11. Aldehydes whenever produced by a process as claimed in any one of the preceding claims.

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Agents for the Applicants.

\* denotes a Registered Trade Mark.

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COMPLETE SPECIFICATION

*This drawing is a reproduction of  
the Original on a reduced scale.*

